

## The Valency Angles of Oxygen and Sulphur

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*(Received for publication, July 2, 1934.)*

### ABSTRACT.

The valency angles of oxygen and sulphur atoms are calculated for a number of simple molecules from their fundamental frequencies of oscillation, and their dipole moments.

### 1. Introduction.

The determination of the relative orientations of the different valency bonds connecting an atom to its neighbours in a molecule is a problem of importance in chemistry. In certain favourable cases, the determination presents no difficulty. For example, in cyclopropane, the angles between any two C—C bonds can be shown from direct considerations of symmetry to be  $60^\circ$ , and similarly in methane or carbon tetrachloride the valency bonds can be shown to make with one another angles of  $109^\circ 5'$ . In other cases, however, the problem presents difficulties, and one has to deduce the angles by indirect methods.

One of the methods in general use for finding the valency angle is based on a knowledge of the permanent dipole moment

of the molecule. As is well-known, with each chemical bond may be associated a definite dipole moment characteristic of the bond. The resultant moment of the molecule as a whole will be the vectorial sum of the moments of the constituent bonds. When the moments of these bonds are known, the magnitude of the resultant moment gives one an idea of the relative orientations of these various bonds. In simple cases, such a correlation may give definite information regarding the angles between the valency bonds.

In the case of simple molecules, there is another method which has been used with success. It has been shown by Bjerrum,<sup>1</sup> Dennison<sup>2</sup> and others that the natural oscillation frequencies of a simple molecule can be calculated from the known dispositions of the atoms and the binding forces between them. Conversely, a knowledge of the oscillation frequencies of a molecule derived from infra-red absorption measurements, or more conveniently from its Raman spectrum, enables one to deduce, in favourable cases, the binding forces and the relative orientations of the chemical bonds.

Both the methods have their natural limitations. The latter method can be applied conveniently in particular to simple triatomic molecules. For more complicated ones the identification of the different observed frequencies as due to a particular mode of oscillation of the molecule becomes increasingly difficult, and the method, therefore, ceases to be of practical value. In the dipole method, on the other hand, a knowledge of the dipole moments characteristic of the constituent chemical bonds is presumed. In most cases, this is not available, and even under favourable conditions, only rough estimates of the characteristic moments of the bonds can be made. The valency angles calculated from these data are naturally uncertain. By a suitable combination of the two methods, it is possible, however, to deduce

<sup>1</sup> N. Bjerrum, *Verh. D. Phys. Ges.*, Vol. 16, p. 737 (1914).

<sup>2</sup> D. M. Dennison, *Phil. Mag.*, Vol. I, p. 195 (1926).

the valency angles with definiteness. In the present paper, the valency angles of oxygen and sulphur are calculated in this manner for a number of simple compounds.

## 2. Oscillations of a Triatomic Molecule.

The calculation of the valency angles from the Raman frequencies is particularly simple in the case of symmetrical triatomic molecules of the type  $XY_2$ , for which the theory has been worked out in great detail by Bjerrum, Dennison and others. The angle between the two  $X-Y$  bonds gives directly the valency angle of the atom  $X$ . From this point of view, several of the molecules considered in this paper have been so chosen that in effect they may be treated as triatomic molecules of the above type.

The simplest molecule of this type has three fundamental oscillation frequencies, say  $\nu_1$ ,  $\nu_2$  and  $\nu_3$  corresponding to oscillations represented in Fig. 1.

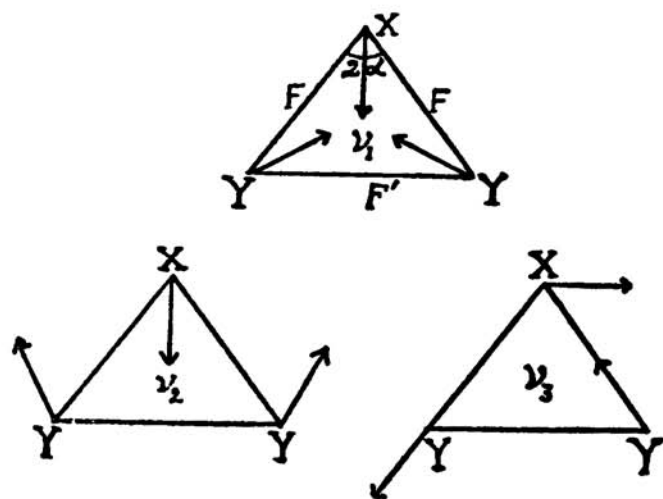


FIG. 1.

Let us denote by  $F$  the binding force between the  $X$  and  $Y$  atoms, and by  $F'$  the force between  $Y$  and  $Y$ , and let  $2\alpha$  be the angle between the two  $X-Y$  bonds. Also let the mass of  $X$  be

M and of Y be  $m$ . Then it can be shown that

$$n_1 = \frac{F}{m} \left[ p + (1-p) \cos^2 \alpha \right] \quad \dots (1)$$

$$n_2 n_3 = \frac{2F'}{m} \times \frac{F}{m} \times p \cos^2 \alpha \quad \dots (2)$$

$$n_2 + n_3 = \frac{2F'}{m} + \frac{F}{m} \left[ 1 - (1-p) \cos^2 \alpha \right] \quad \dots (3)$$

$$\text{where } p = \frac{M+2m}{M}; \quad n^2 = \frac{4\pi^2 c^2}{L} \nu^2. \quad \dots (4)$$

If the three fundamental frequencies  $\nu_1$ ,  $\nu_2$  and  $\nu_3$  are known, the three equations enable us to calculate  $F$ ,  $F'$  and  $2\alpha$ .

### 3. Dimethyl Ether.

We shall first consider dimethyl ether. In view of the small mass of the three hydrogen atoms in the methyl groups, we may treat the methyl groups as single units of mass 15. The molecule of dimethyl ether can then be considered as a triatomic molecule of the type discussed above.  $2\alpha$  in this compound will naturally denote the angle between the two C—O bonds, and will, therefore, give the valency angle of the oxygen atom in the compound. In order to calculate  $\alpha$ , we require to know the three  $\nu$ 's. From the Raman spectrum the three fundamental frequencies of the  $(\text{CH}_3)_2\text{O}$  molecule are found to be

$$1106 (3); \quad 921 (4); \quad 267 (1).$$

From these frequencies, using the relations (1) to (3) we obtain, in the first place, for  $F$ , *i.e.*, for the binding force between C and O, the value 4.52 dyn/cm., and for  $F'$ , the binding force between C and C, the value 0.68 dyn/cm.  $F'$  is naturally much smaller than  $F$  since there is no chemical binding, in the ordinary sense, between the C atoms.

The same equations give for  $2\alpha$ , *i.e.*, for the valency angle of the O atom, the value  $118^\circ$ .

#### 4. Dipole Moment of the C—O Bond.

The dipole moment of  $(\text{CH}_3)_2\text{O}$  has been measured by Sanger and Steiger,<sup>3</sup> and Stuart,<sup>4</sup> and they obtain the value 1.32D and 1.29 D respectively ( $\text{D} = 10^{-18}$  c.g.s. e.s.u.). Since we know from the previous section the inclination of the two C—O bonds to each other, we can calculate the value of the permanent moment characteristic of either of the C—O bonds. Thus, we obtain

$$\mu_{\text{C-O}} = \frac{1.29 \times 10^{-18}}{2 \cos 59^\circ} = 1.25 \text{ D.}$$

#### 5. Diethyl, Dipropyl and Diphenyl Ethers.

The calculation of the valency angle of O in these compounds from their Raman frequencies is not rigorous in view of the complicated structure of the  $(\text{C}_2\text{H}_5)$  group, which we cannot treat as a single oscillating unit. However, since we know the dipole moment of  $(\text{C}_2\text{H}_5)_2\text{O}$  and also the moment of the C—O bond we can readily calculate the angle between the two C—O bonds. We thus obtain

$$2\alpha = 2 \cos^{-1} \cdot \frac{1.14}{2 \times 1.25} = 126^\circ.$$

This value is larger than that obtained for  $(\text{CH}_3)_2\text{O}$ , and is evidently due to the larger size of the  $(\text{C}_2\text{H}_5)$  groups, which would tend to open out the two C—O bonds.

The dipole moment<sup>5</sup> of  $(\text{C}_6\text{H}_5)_2\text{O}$ , *viz.*, 1.16 D, gives in the same manner for the valency angle of oxygen  $124^\circ.8$ , which is practically the same as the value in  $(\text{C}_2\text{H}_5)_2\text{O}$ . No dipole moment data are available for higher members of this series.

<sup>3</sup> 'Helv. Phys. Acta,' Vol. 2, p. 136 (1929).

<sup>4</sup> Z. Physik, Vol. 51, p. 490 (1928).

<sup>5</sup> Meyer and Buchner, 'Physikal. Z.,' Vol. 33, p. 390 (1932).

We may consider in this section also the case of diphenyl ether  $(C_6H_5)_2O$ , whose permanent moment has recently been measured by Bergmann and Tschudnowsky,<sup>6</sup> and is found to be 1.12 D. If the characteristic dipole strength of the C—O bond in this compound is the same as in the aliphatic ethers considered in the previous paragraphs, this value of the dipole moment of  $(C_6H_5)_2O$  would correspond to a valency angle of

$$2 \cos^{-1} \left( \frac{1.12}{2 \times 1.25} \right) \text{ or } 127^\circ$$

for the O atom. This is the same as in the other compounds considered.

## 6. Water.

In order to make the series of triatomic molecules of the type  $OY_2$  complete, we shall include also the simplest molecule of this type, *viz.*,  $OH_2$ . The structure of this molecule has been discussed in detail by a number of workers from various independent points of view, among whom may be specially mentioned Debye,<sup>7</sup> Hund<sup>8</sup> and Mecke<sup>9</sup> and his collaborators. By an extensive critical analysis of the rotation vibration spectrum of this molecule, Mecke has recently determined accurately the three moments of inertia of the molecule in the ground state, *viz.*,  $I = 0.995 \times 10^{-40}$ ,  $L = 1.908 \times 10^{-40}$  and  $K = 2.980 \times 10^{-40}$ . The relation  $I+L=K$  is nearly satisfied. For the oscillationless state, Mecke obtains by extrapolation the values  $I = 1.009 \times 10^{-40}$ ,  $L = 1.901 \times 10^{-40}$  and  $K = 2.908 \times 10^{-40}$ . These values satisfy accurately the relation  $I+L=K$ . From these data, the valency angle of oxygen comes out as  $104^\circ$ - $106^\circ$ .

On the other hand, Plyler,<sup>10</sup> who has discussed in great detail the infra-red absorption bands of water, adopts the follow-

<sup>6</sup> 'Z. Phys. Chem.,' B, Vol. 17, p. 107 (1932).

<sup>7</sup> "Polar Molecules," The Chemical Catalog Co., Inc., 1929, Chap. IV.

<sup>8</sup> Hund, 'Z. Physik,' Vol. 31, p. 81 (1925); Vol. 32, p. 1 (1925).

<sup>9</sup> 'Z. Physik,' Vol. 81, p. 465 (1933).

<sup>10</sup> Plyler, 'Physic. Rev.,' Vol. 89, p. 77 (1932).

ing three as the fundamental frequencies of oscillation of the  $\text{H}_2\text{O}$  molecule, viz.,  $\nu_1 = 5309 \text{ cm}^{-1}$ ,  $\nu_2 = 1597 \text{ cm}^{-1}$  and  $\nu_3 = 3742 \text{ cm}^{-1}$ . From these frequencies, using Dennison's formulae (1), (2) and (3) above, he obtains for the valency angle  $2\alpha$  of the oxygen atom the value  $115^\circ$ .

### 7. The Valency Angle of Oxygen.

We may collect in this place the values obtained for the valency angle of oxygen in various compounds. They are given in Table I.

TABLE I.

Molecule.	Method.	Valency Angle of Oxygen.
$\text{H}_2\text{O}$	Plyler from oscillation frequencies	$115^\circ$
	Mecke from Rotation-Vibration Spectra	$104^\circ\text{--}106^\circ$
$(\text{OH})_2\text{O}$	From Raman frequencies	$118^\circ$
$(\text{C}_2\text{H}_5)_2\text{O}$	From $\mu = 1.12 \text{ D}$	$125^\circ.8$
$(\text{C}_3\text{H}_7)_2\text{O}$	From $\mu = 1.16 \text{ D}$	$124^\circ.8$
$(\text{C}_6\text{H}_5)_2\text{O}$	From $\mu = 1.12 \text{ D}$	$126^\circ.9$

The values group about  $120^\circ$ .

### 8. Ethylene Oxide.

We next consider the simple heterocyclic compound containing oxygen, viz., ethylene oxide, which also can be treated as a symmetrical triatomic molecule of the type  $\text{AX}_2$ . The heterocyclic nature of this compound in contrast with the open structure of dimethyl ether, is plainly responsible for the wide difference in properties of these two compounds. Let us first consider their Raman spectra. The scattering of ethylene oxide

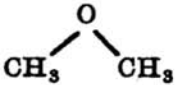
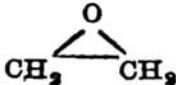
has been studied by the present writer,<sup>11</sup> and its Raman lines are found to be much more intense than those of  $(\text{CH}_3)_2\text{O}$ . Further the fundamental oscillation frequencies are found to be 865, 810 and  $1123\text{ cm}^{-1}$ , from which the binding force  $F$  between C and O atoms, and the force  $F'$  between two C atoms as also the valency angle  $2\alpha$  of O can be calculated as before. Doing so, we obtain

$$F = 4.2 \times 10^5; \quad F' = 3.4 \times 10^5;$$

$$\text{and } 2\alpha = 64^\circ.$$

These values are of interest, especially when viewed in relation to the corresponding values for  $(\text{CH}_3)_2\text{O}$ . The values for the two compounds are placed together in the following Table for comparison:—

TABLE II.

Compound.	$F \times 10^{-5}$ .	$F' \times 10^{-5}$ .	Valency Angle.
	4.5	0.68	118°
	4.2	3.4	64°

$F$  is practically the same for the two compounds.  $F'$ , however, is much larger in  $(\text{CH}_3)_2\text{O}$  than in  $(\text{CH}_2)_2\text{O}$ . This is what we should expect because of the presence of a chemical bond between the two C atoms in  $(\text{CH}_2)_2\text{O}$ , which is absent in  $(\text{CH}_3)_2\text{O}$ . This C—C bond in  $(\text{CH}_2)_2\text{O}$  will naturally tend to bring the two C atoms close together, so that the valency angle of O should be much smaller in this compound than in  $(\text{CH}_3)_2\text{O}$ . This, as we see from Table II, is actually the case, the valency

<sup>11</sup> To be published elsewhere.



angles of O in the two compounds being  $64^\circ$  and  $118^\circ$  respectively.

This large difference in the valency angle in the two compounds will also mean a corresponding difference in their dipole moments. The dipole moment of  $(\text{CH}_3)_2\text{O}$  is not only much greater than that of  $(\text{CH}_3)_2\text{S}$ , but the ratio between the two moments, viz.,  $\frac{1.88}{1.29} = 1.5$ , has nearly the same value as

$$\frac{\cos 32}{\cos 59} = 1.6. \quad \text{This shows that the characteristic dipole}$$

moment of the C—O bond is practically the same in the two compounds in spite of differences in the nature of the C—O bonds in the two compounds.

### 9. Dimethyl Sulphide.

Among the simple sulphur compounds  $(\text{CH}_3)_2\text{S}$  would be very suitable for direct calculation of the valency angle. The Raman Spectrum of this compound has been recently studied by the present writer. Treating this molecule as a triatomic one of the type  $\text{AX}_2$ , the natural frequencies of oscillation as given by their Raman spectra are as follows :

$$\nu_1 = 694 (8), \quad \nu_2 = 745 (5), \quad \nu_3 = 284 (6).$$

From these values, the valency angle of S, viz.,  $2\alpha$ , comes out as  $100^\circ$ .

### 10. Other Sulphur Compounds.

From the above value of  $2\alpha$ , and the known dipole moment<sup>12</sup> of  $(\text{CH}_3)_2\text{S}$ , viz., 1.41, the value of the moment characteristic of C—S bond comes out as 1.09 D (which is practically the same as for the C—O bond). Using this value, we can now

<sup>12</sup> Hunter and Partington, J. O. S., p. 2812 (1932).

calculate in the same manner as we did for the ethers, the valency angle of S in diethyl, dipropyl and other sulphides. The following table gives the values so obtained :—

TABLE III.

Compound.	Method.	Valency angle of S.
H <sub>2</sub> S	From infra-red frequencies	90°
(CH <sub>3</sub> ) <sub>2</sub> S	From Raman frequencies	100°
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> S	From dipole moment	87°·8
(C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> S	"	89°·4
(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> S	"	87°·8
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> S	"	95°·2

Thus in all the compounds, the angle is near about 90°, and is considerably smaller than that of O in the corresponding oxygen compounds.

The author desires to express his grateful thanks to Prof. K. S. Krishnan, D.Sc., for the keen interest he took during the progress of this work.